418

PLASTIC FLOW PROPERTIES OF CASEIN [1,2]

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Introduction

The flow properties of casein during extrusion and molding are important to the manufacturer of casein plastic. Variations in flow due to differences in the quality of caseins or other factors produce undesirable variations in the product. Several papers have dealt with flow characteristics of casein plastics. Cooper and Hand (1) have described a test for quality control of rennet casein in which a Scott Plastomoter was used. Haller (2) demonstrated a relationship of flow to pressure and water content at room temperature. He found that there was a sudden increase of flow when the water content was increased to 20–21%, which he considered to be caused by a change in the structure of the casein gel. The effect of different pH, and ash and lactose contents on plastic flow was studied by Gallay and Tapp (3), who extruded casein with a laboratory extruder at pressures from 20,000 to 77,000 p.s.i.

It appeared desirable to extend the study on the flow properties of casein to include pressures and temperatures nearer to those generally employed in the manufacture of casein plastics and to compare the flow properties of acid casein with those of rennet casein and modified caseins.

Materials and Testing Procedure

For testing the effect of composition of casein on flow properties the following samples of casein were used:

(*1*). *High-grade commercial acid casein containing 0.67% ash.*[4]

(*2*). *Commercial rennet casein containing 8.5% ash.*

(*3*). *Rennet casein prepared from acid casein by the following method:* 500 g. of acid casein was dissolved with sodium hydroxide in 17 l. of water. Water solutions containing 32 g. of calcium hydroxide

[1] Presented at the Annual Meeting of the Society of Rheology, New York, N. Y., November 4–5, 1949.

[2] A contribution from the Eastern Regional Research Laboratory, one of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Dept. of Agriculture.

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[4] All ash values are on a moisture-free basis.

and 53 g. of dihydrogen calcium phosphate were added simultaneously with rapid stirring in order to obtain a colloidal dispersion of insoluble calcium phosphate in the casein solution. The resulting solution contained about the same amount of casein, calcium, and phosphorus as skim milk. The final pH of the solution was adjusted to 6.7 with dilute hydrochloric acid. To this solution was added 0.35 g. of Hansen's rennet. After coagulation, the mixture was heated to 40°C. and the casein was filtered, washed, and dried at 50°C. The ash content of this casein was 13.5%.

(*4*). *Para casein prepared from acid casein by the following method:* 600 g. acid casein was dissolved in sodium hydroxide and diluted to 15 l. with water. Calcium chloride (95 g.) was added, and the pH was adjusted to 6.7. The solution was clotted by the addition of 0.5 g. Hansen's rennet. After clotting, the casein was filtered, washed, dissolved in sodium hydroxide, and diluted to 15 l. The casein was precipitated by adding dilute hydrochloric acid to pH 4.6, washed free of chloride ions, and dried at 50°C. The ash content was 1.3%.

(*5*). *Carbamido casein* prepared and described by Hipp *et al.* (4): by treating casein with potassium cyanate.

(*6*). *Reprecipitated commercial acid casein.*

To determine whether dissolving and reprecipitating affect the flow properties of casein, a sample was prepared by dissolving acid casein in dilute sodium hydroxide and precipitating with hydrochloric acid. After the casein was filtered and washed, it was dried at 50°C.

The Rossi-Peakes flow tester (5), a constant-force, vertical-orifice type machine was used to determine plastic flow. The Rossi-Peakes apparatus was chosen for this work because (*1*) the measurements of plastic flow are obtained under dynamic conditions, (*2*) temperature and pressure are easily adjusted to obtain measurable plastic flow with reasonable variations in water content, (*3*) the measurement is made within an enclosed chamber which prevents the loss of moisture, and consequently the plastic flow value is obtained on material with a constant moisture content, (*4*) the actual flow measurement requires only 2 min., which minimizes the changes in physical properties that occur in different degree when casein is heated in the dry state or in the presence of moisture, and (*5*) the results are precise and highly reproducible. The Rossi-Peakes machine is substantially free of the kneading or shearing action present in commercial extruders for casein plastics.

The test specimen, a cylinder $\frac{3}{8}$-in. in diameter and $\frac{3}{8}$-in. in height, was made at room temperature on a hand-operated tablet machine. It was found that a variation in the density of the test specimen between the weights of 0.70–0.75 g. for a roughly constant volume did not measurably affect the plastic flow. The plastic material under the influence of heat and pressure was forced into an orifice $\frac{1}{8}$-in. in diameter and 2 in. long. The distance of flow into the orifice was measured by a follower rod and was recorded on a time graph with a mechanical ratio of 3:1. By this device the plastic flow can be precisely measured to $\pm$ 0.01 in.

For normal operation of the flow tester at 100°C. or higher, steam at the required pressure was circulated in passages around the orifice and the material chamber. By the use of two pressure-regulating valves, the temperature within a series was maintained within $\pm$ 0.2°C. For temperatures below 100°C., hot water from a thermostatically controlled, electrically heated water bath was circulated by means of a centrifugal pump.

Experimental

In testing the plastic flow of casein, it is difficult to keep the water content of the test specimens constant because samples lose water by evaporation during their preparation. Samples were prepared as follows: to the ground casein, water was added in amounts that gave the approximate water content desired. The moistened casein was sifted through a 40-mesh sieve and placed in a closed container. A portion of the moistened casein was made into pellets by use of a tablet press and then placed back in the container with the moistened ground casein and allowed to equilibrate in the refrigerator for 6–7 days. The exact water content of the pellets was determined at the same time as the flow test by drying them at 105°C. for 3 hr. or more, or until they reached constant weight. In all cases, the water content of the test specimen was in equilibrium with the powdered casein.

The caseins tested for plastic flow at various water contents are listed in Tables I and II; the measurements are the average of three closely checking values. The tests were performed at temperatures from 50 to 140°C. and pressures of 500–3000 p.s.i. For each water content, the plastic flow can be expressed as a function of either pressure or temperature. Figures 1 and 2 are graphs for commercial acid casein with a 19.10% water content. The plastic flow in this instance is defined as the distance the material is forced into the orifice during a period of 2 min. It is not possible to compare the flow properties of two caseins by means of these curves alone, since the water content of each sample differs because of experimental difficulties, and the relation between the water content and flow is unknown. The American Society for Testing Materials term "flow temperature" has been adopted. They define the flow temperature (6) as the temperature at which the material flows 1 in. when subjected to a pressure of 1500 p.s.i. over a period of 2 min. For our work, however, it was necessary to modify this definition in order to cover a reasonable range of the three parameters—temperature, pressure, and water content. The tem-

TABLE I

Plastic Flow Measurements of Commercial Type Caseins

Water content	Temperature	Pressure of (p.s.i.)					
		500	1000	1500	2000	2500	3000
		***(1)* Commercial acid casein**					
per cent	*°C.*	*in.*	*in.*	*in.*	*in.*	*in.*	*in.*
8.70	110	—	—	—	—	—	0.10
	120	—	—	—	—	—	0.21
	130	—	—	0.17	—	—	0.50
	140	—	—	0.28	0.42	0.60	0.88
	150	—	—	0.38	0.75	1.09	1.43
13.00	100	—	—	0.18	0.25	0.34	0.43
	110	—	0.21	0.37	0.55	0.70	0.90
	120	—	0.36	0.62	0.90	1.31	—
	130	0.10	0.40	1.05	—	—	—
	140	0.16	1.40	—	—	—	—
15.20	80	—	—	0.15	—	—	0.39
	90	—	0.17	0.27	0.36	—	0.55
	100	—	0.24	0.42	0.52	0.74	0.86
	110	0.10	0.32	0.55	0.70	1.02	1.58
	120	0.22	0.68	1.40	—	—	—
19.10	70	—	—	0.25	0.40	0.51	0.61
	80	—	0.25	0.40	0.55	0.70	0.95
	90	0.15	0.42	0.64	0.92	1.19	1.52
	100	0.20	0.59	1.03	1.55	—	—
	110	0.32	0.90	—	—	—	—
27.50	50	—	0.30	0.50	0.83	1.10	1.35
	60	0.20	0.57	0.93	1.30	—	—
	70	0.48	1.05	—	—	—	—
	80	0.95	—	—	—	—	—
		***(2)* Commercial rennet casein**					
10.60	110	—	—	0.18	—	0.27	0.33
	120	—	—	0.21	0.26	0.36	0.44
	130	—	—	0.27	0.40	0.55	0.70
	140	—	—	0.44	0.70	0.86	1.19
	147.5	—	—	—	0.92	1.16	1.50
13.25	102	—	—	0.22	0.30	0.40	0.46
	106	0.12	0.22	0.35	0.42	0.50	0.62
	110	0.14	0.25	0.35	0.50	0.61	0.70
	120	0.14	—	0.50	0.68	0.92	—
	130	0.17	—	0.67	1.22	—	—

TABLE I—*Continued.*

Water content	Temperature	Pressure of (p.s.i.) 500	1000	1500	2000	2500	3000
		(2) Commercial rennet casein					
per cent	°C.	*in.*	*in.*	*in.*	*in.*	*in.*	*in.*
15.00	100	—	0.40	0.65	0.85	1.03	1.20
	105	—	0.47	0.73	1.00	1.30	—
	110	—	0.56	0.90	1.20	—	—
	115	0.22	0.68	1.05	—	—	—
	120	0.28	0.76	1.39	—	—	—
19.40	70	—	—	0.33	0.45	0.56	0.70
	80	0.15	0.40	0.58	0.82	1.20	—
	90	0.20	0.50	0.82	1.30	—	—
	100	0.40	0.95	—	—	—	—
23.25	60	—	0.32	0.42	0.55	0.70	0.87
	70	—	0.50	0.68	0.92	1.32	—
	80	—	0.72	1.43	—	—	—
	90	0.37	1.00	—	—	—	—
27.90	40	—	0.15	0.28	0.40	0.50	0.60
	50	—	0.28	0.43	0.70	0.87	1.08
	60	0.20	0.40	0.90	1.10	—	—
	70	0.35	1.10	—	—	—	—
		(3) Laboratory-prepared rennet casein					
14.30	100	—	0.19	0.30	0.38	0.48	0.61
	110	0.15	0.32	0.65	0.91	1.05	1.15
	120	0.15	0.45	0.92	1.23	—	—
18.70	70	—	—	0.30	0.38	0.49	—
	80	—	—	0.33	0.63	0.78	1.00
	84	—	0.46	0.97	1.12	—	1.46
22.90	60	—	—	0.43	0.64	0.78	1.00
	70	0.20	0.53	0.80	1.20	—	—
	80	0.40	0.95	—	—	—	—

perature where the casein flows 0.75 in. under the same conditions was used as the "flow temperature."

To determine flow temperatures for the caseins at the various water contents in Tables I and II, the flow at the pressure of 1500 p.s.i. is plotted against temperature. The data for acid casein are presented in Fig. 3.

TABLE II

Plastic Flow Measurements of Modified Casein

Water Content	Temperature	Pressure of (p.s.i.)	
		1500	2000
(4) Para casein			
per cent	°C.	*in.*	*in.*
13.50	115	0.75	1.00
16.70	71	0.25	0.32
	78	0.38	0.60
	84	0.62	0.90
	88	0.95	1.11
20.80	61	0.30	0.40
	71	0.70	0.90
	84	1.04	1.28
(5) Carbamido casein			
14.00	110	0.45	
	116	0.76	
	123.5	0.92	
17.50	85	0.67	
	101	1.16	
	111	1.40	
21.50	50	0.19	
	67	0.70	
	73	0.90	
27.50	50	0.70	
	56.5	0.93	
	67	1.30	
(6) Reprecipitated acid casein			
14.00	115	0.40	0.57
	121	0.60	0.90
	132	0.90	1.40
16.30	100	0.44	0.65
	105	0.62	0.81
	113	0.98	1.16
23.20	61	0.30	0.50
	71	0.65	1.00
	78	0.96	—

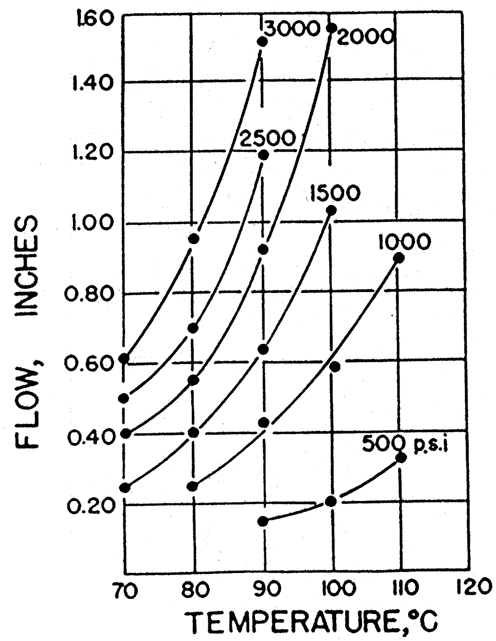

FIG. 1. Effect of temperature on plastic flow of commercial acid casein with 19.10% water content at various pressures.

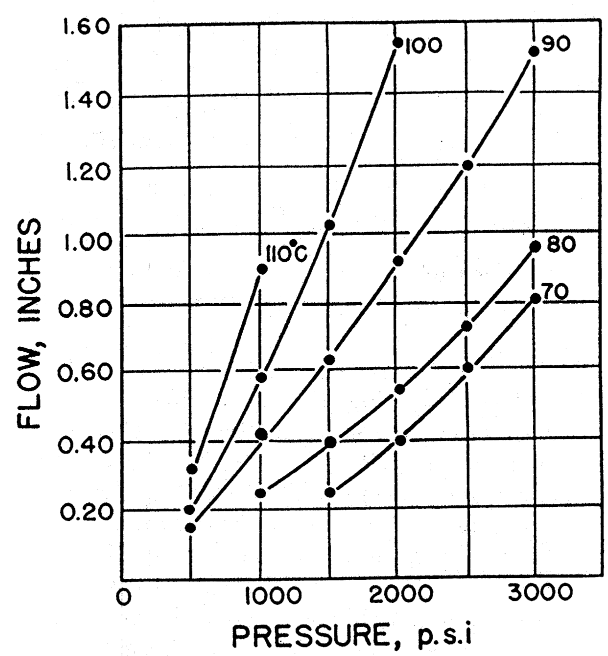

FIG. 2. Effect of pressure on plastic flow of commercial acid casein with 19.10% water content at various temperatures.

Figure 4 shows the effect of water content on the flow temperature for all the caseins studied. The tridimensional graph in Fig. 5 shows the temperature, pressure, and water-content relationship required to obtain a flow of 0.75 in. for commercial rennet casein. The values on the temperature axis are the temperatures required to give a flow of 0.75 in. at the indicated pressures and water content, and are not to be confused with "flow temperature," which refers to a fixed pressure of 1500 p.s.i. The data for Fig. 5 are obtained from families of curves (shown for example in Fig. 1, which gives the data for a single water content) by reading the temperature required to obtain a flow of 0.75 in. at each pressure. Similarly, the

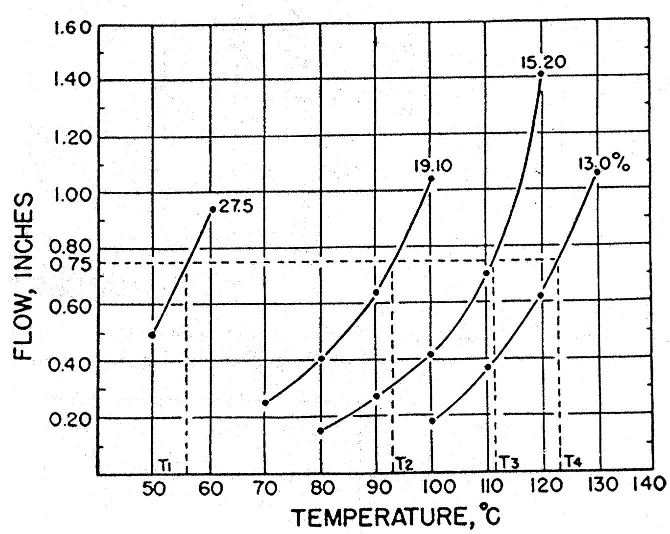

FIG. 3. Effect of temperature on plastic flow of commercial acid caseins with various water contents at 1500 p. s. i. T_1, T_2, etc., are the "flow temperatures."

data for each water content are obtained from the isobars. A few of the values in Fig. 5 were obtained from extrapolated curves.

Discussion of Results

The data in Fig. 4 show that there are no great differences between the flow temperature-water content plots for the caseins studied, and therefore one may conclude that, for industrial use, difficulties arising from uneven flow may be overcome by altering the water content or the extrusion temperature. None of the data shows the sudden rise in plastic flow at 20–21% water content recorded by Haller (2). The apparent deviation from a smooth curve at 13.25 and 15.00% water content for rennet casein shown in Fig. 5 may be due to a chemical change of the protein induced by temperatures above 110°C. The rate at which the flow temperature in-

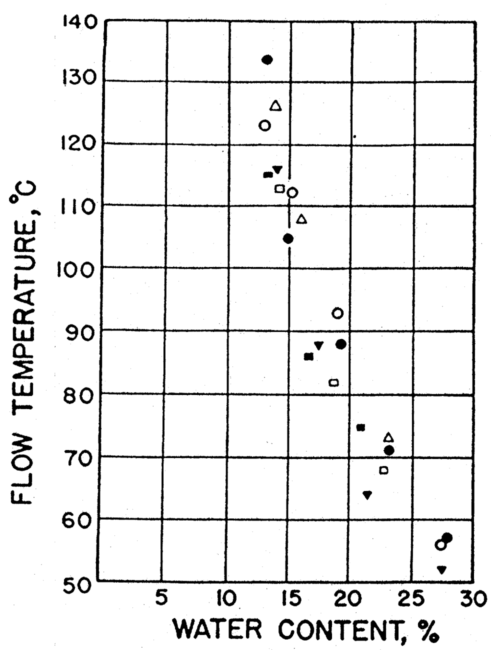

Fig. 4. Flow temperature for caseins of different water contents. ○ Commercial acid casein; ● commercial rennet casein; □ laboratory-prepared rennet casein; ■ para casein; △ reprecipitated acid casein; ▼ carbamido casein.

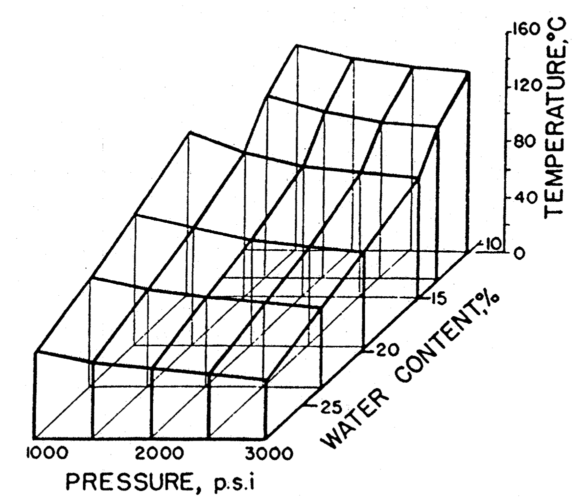

Fig. 5. Temperature, pressure, and water content required to give a plastic flow of 0.75 in. for commercial rennet casein.

creases at water contents lower than 15% is much greater than the rate of change at water contents above 15% (Fig. 4). Figures 1 and 2 show that the rate of increase in the plastic flow at a given water content increases with temperature and with pressure. The combined effect of temperature and pressure in relation to water content to produce a given plastic flow is shown in Fig. 5.

Our results on flow properties of casein are consistent with those of Gallay and Tapp (3), but greatly extend their measurements with respect to temperature and water content. By extending the temperature from that of the room to a range of 50–140°C., the flow data may be applied directly to commercial practice.

Although rennet casein is favored in the manufacture of casein plastics, the results on flow properties do not reveal significant differences between rennet and high-grade acid caseins. Any superiority of rennet casein due to desirable flow properties can be obtained with acid casein by minor changes in the water content or temperature of extrusion.

Summary

Plastic flow measurements of commercial and laboratory-prepared caseins were made with the Rossi-Peakes flow tester. Flow properties of casein samples containing different amounts of moisture were determined at temperatures from 50° to 140°C and pressures from 500 to 3000 p.s.i. Only minor differences were found in the "flow temperature." The transition in flow properties, corresponding to a water content of about 21%, as described by Haller, could not be demonstrated. A tridimensional graph for rennet casein is presented which illustrates the temperature, pressure, and water-content requirements necessary to obtain a given plastic flow.

References

1. Cooper, C. A., and Hand, P. G. T., *Brit. Plastics* **10**, 572–77 (1939).
2. Haller, W., *Kolloid-Z.* **57**, 197–203 (1931).
3. Gallay, W., and Tapp, J. S., *Can. J. Research* **16B**, 345–60 (1938).
4. Hipp, N. J., Groves, M. L., Swain, A. P., and Jackson, R. W., *Modern Plastics* **26**, 205 (Sept., 1948).
5. Rossi, L. M., and Peakes, G. L., assignors to Bakelite Corp., U. S. Patent 2,066,016, Dec. 29, 1936.
6. "Tentative method of test for measuring flow temperature of thermoplastic materials," A. S. T. M. Designation D569–44T.